

NEW RESULTS IN ELECTROLYSIS.

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(Contribution from the John Harrison Laboratory of Chemistry.)

Since it was observed that anions could readily be estimated by means of the mercury cathode and rotating anode (*Jr. Amer. Chem. Soc.*, 29, 447), the thought occurred that anions might also be separated by the same means. With this end in view, the following study was undertaken. Potassium ferrocyanide and potassium ferricyanide were the salts used in the work. It was decided to conduct experiments in order to find any difference which might exist in the decomposition pressures. If such conditions did exist, then separations might be effected by this procedure.

The experiments were carried out in the same apparatus and following the directions given in the paper mentioned above. A solution of potassium ferrocyanide, containing in 50 c.c., 0.1316 gram of the salt, under a pressure of 4.5 volts and a current of 0.15 ampere at the beginning, falling to 0.02 ampere at the end, in one hour gave the total $\text{Fe}(\text{CN})_6$ present. This was equal to 0.0661 gram. The ferricyanide solution, containing 0.1070 gram of the salt, equivalent to 0.0636 gram of $\text{Fe}(\text{CN})_6$, was subjected to the same current, giving the required amount of anion in about the same period of time.

When trying the effect of lower currents, for example 1.5 volt and 0.07–0.02 ampere, upon potassium ferricyanide, it was observed that there was no decomposition of the amalgam in the outer cell. But when phenolphthalein was added to the contents of the inner cell, a strong alkaline reaction was indicated. The silver anode had increased 0.0467 gram after an hour's action of the current, while the amount of potassium present was only 0.0156 gram instead of 0.0253 gram, the equivalent quantity. It was decided to repeat

this work later and to seek for an explanation of its discrepancy, and in the meantime to ascertain the effects of lower currents upon both potassium ferrocyanide and potassium ferricyanide.

A thermopile was used as the source of the current in all the subsequent work. A water rheostat was constructed from a battery jar about twelve inches high by 9" by 6" cross section, containing a dilute solution of sodium chloride in which were immersed two lead plates six inches square. The resistance was regulated by raising or lowering the plates in the solution. The voltmeter, graduated to one thirtieth of a volt, and the milliammeter were continually in the circuit.

Potassium ferrocyanide was acted upon by a current of 0.4 volt. This gave a current unappreciable on the milliammeter. It acted for an hour and a quarter. There was no decomposition observed in the outer cell. Titration of the contents of the inner cell with N/10 hydrochloric acid showed the presence of 0.0039 gram of potassium. The anode increased in weight by 0.0052 gram. This is in about equivalent quantities. (The theoretical equivalent of potassium would be 0.00382 gram.) By using a current of 0.13–0.16 volt, there was no evidence of decomposition, either in increase in the weight of the anode or evidence of potassium hydroxide in either cell, with phenolphthalein as indicator. Even 0.02 volt in one hour had not effected any change, but with 0.23 volt, the anode, after an hour's action of the current, had increased 0.0004 gram, and a faint pink color was observed when phenolphthalein was added to the solution in the inner cell. This was dispelled by a fraction of a drop of N/10 hydrochloric acid. With a current of 0.266 volt, the anode after the same period of time had increased 0.0014 gram. When 0.3 volt was employed 0.0022 gram of $\text{Fe}(\text{CN})_6$ had separated on the anode and 0.00039 gram of potassium was found in the solution. A current of 0.4 volt showed 0.005 gram of $\text{Fe}(\text{CN})_6$ and 0.00107 gram of potassium, while 0.5 volt gave 0.0064 $\text{Fe}(\text{CN})_6$ and 0.0041 gram of potassium.

The following table shows the effect of increase in the current :

Current in Volt.	Fe(CN) ₆ in Gram.	Potassium in Gram.
0.23	0.0004
0.266	0.0014
0.3	0.0022	0.00039
0.4	0.005	0.00107
0.5	0.0064	0.0041
0.66	0.0073	0.0054
0.83	0.0164	0.01209
1.0	0.0174	0.0117

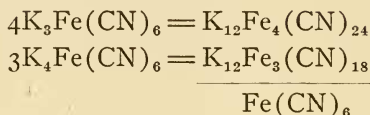
The milliammeter in the last two experiments showed a current of one milliampere at the beginning, which at the end had fallen to 0.0005 ampere.

There appears therefore to be no decomposition of potassium ferrocyanide by currents lower than 0.23 volt.

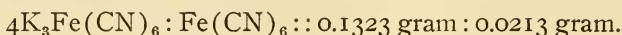
Experiments were then conducted in order to ascertain the effects of low currents upon potassium ferricyanide. The salt used was recrystallized several times. The solution contained 0.1323 gram of the salt. This was equivalent to 0.0471 gram of potassium and 0.0852 gram of Fe(CN)₆. There was no evidence of potassium hydroxide in either cell after the current, having an electromotive force of 0.3 volt and 0.5 milliampere, had acted for half an hour. With 0.66 volt, giving a current of 0.002 ampere at the beginning of the experiment acting for an hour, the anode increased 0.0309 gram in weight and but 0.0039 gram of potassium was found. These experiments confirmed the observations made upon potassium ferricyanide at the beginning of the work. The increase in weight of the anode was out of proportion to the amount of potassium present. Several other experiments with low currents gave similar results. For example, a current of 0.4 volt, after one half hour's action of the current showed only a small amount of potassium but 0.0279 gram of Fe(CN)₆. When a current of 0.1 volt was passed, the anode, after an hour's action of the current, increased 0.0223 gram, but there was no evidence of potassium hydroxide in the solution.

An explanation of these results was sought. As the solution changed color, and showed the presence of ferrocyanide on testing with ferric chloride, after electrolysis, it was thought that ferricyanide might first be reduced to ferrocyanide. Four molecules of

ferricyanide would form three molecules of ferrocyanide with the splitting off of one radical, thus :



This would therefore give



By constant and careful observation of the voltmeter, it was thought the end of this reaction could be detected.

In the first experiment with this end in view, a current of 0.4 volt and 0.001 ampere was passed through the solution of potassium ferricyanide. There was a constant tendency of the voltage to rise. But by throwing in resistance this was maintained at 0.4 volt, the current falling to 0.0002 ampere. In about thirty minutes the voltage was observed to fall slightly. The current was then interrupted. The anode had increased 0.0217 gram and there was no potassium hydroxide detected in either cell. Subsequent experiments, carrying out the same plan, gave 0.0211, 0.0214, 0.0209, 0.0213 gram increase in weight of the anode. The operations required constant and careful attention, inasmuch as the point at which the change takes place is momentary. The speed of the anode in all cases was about seventy-four revolutions per minute. The time required for the reaction varies slightly with the conditions, as may be observed from the following table :

Current in Ampere.	Volts.	Time in Minutes.	Fe(CN) ₆ in Gram.
0.001-0.0002	0.4	30	0.0217
0.001-0.0002	0.4	30	0.0211
0.001-0.0002	0.36-0.4	35	0.0214
0.001-0.0002	0.4	35	0.0209
0.002-0.0002	0.4	22	0.0228 (trace of K)
0.002-0.0005	0.4	19	0.0208
0.002-0.0005	0.4	19	0.0213

It therefore seems probable that potassium ferricyanide is at first reduced to ferrocyanide by the current.

That reduction should occur at the anode or in the anode compartment is anomalous. It would perhaps be better to say that a potassium amalgam had formed and in its decomposition hydrogen had caused the reduction of the ferricyanide.

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